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Feasibility of Uranium Detection and Characterization Through Container Walls using Ultrahigh Energy X-ray Fluorescence

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Introduction:

The quantitative analysis of uranium in spent nuclear fuel is at best a challenging task for even the specialized laboratories designed to handle such materials. The reason this measurement is important is the need to account for all nuclear materials under the control of international safeguards agreements. While there are existing methods employed for this measurement, efforts to improve the accuracy of nuclear material accountability are of continuing interest. A new approach for making such measurements involves ultrahigh energy X-ray fluorescence (UHEXRF). UHEXRF is defined in this application as XRF above 80 keV. While there have been works which have explored the use of high energy XRF, almost all these works have dealt with XRF below 80 keV [1]. The appeal of using UHEXRF for quantitative analysis of uranium in spent nuclear fuel is primarily focused on the high penetrating X-rays of the fluorescent radiation [2]. In the case of uranium, the $K\alpha$ line is at 98.428 keV with an absorption edge energy of 115.591 keV. At these energies, both the exciting and fluorescent radiation can penetrate significant shielding. In this particular case, the Zircaloy (zirconium metal alloy) cladding of nuclear fuel rods provides a significant barrier to most spectroscopic elemental analysis methods. In the case of uranium, the calculated penetration depth is on the order of several hundred micrometers into a UO_2 nuclear fuel pellet after penetrating a 600 micrometer thick Zircaloy cladding wall. The depth penetration as well as wall penetration offers a unique opportunity to measure the uranium nondestructively through the container walls with typical XRF accuracy and precision. The ability to measure the U content directly through the container wall offers simple analytical protocol as there would be no sample preparation, direct measurement of the analyte and reduced matrix and mineralogical effects. In addition, at this high energy for XRF, there are few if any line overlaps which simplifies the spectrometry measurements. With a spatially resolved excitation X-ray beam, spatially resolved elemental distributions within the fuel rod, whether it is fresh nuclear fuel or spent nuclear fuel, can be obtained nondestructively. This work will present the feasibility of UHEXRF for qualitative and quantitative elemental analysis of uranium in nuclear fuel surrogates and demonstrate nondestructive, through container wall analyses.

Materials and Methods:

The samples used in this study were created in the laboratory using depleted uranium solutions from a stock 10,000 $\mu\text{g/mL}$ commercial standard. The samples were prepared by depositing known concentrations with a pipet, typically 1 μL , onto a Kapton film substrate. Two types of samples were prepared; one was an acidified aqueous based matrix with known uranium concentrations while the second set was spiked into a synthetic spent fuel (SSF) matrix. The SSF matrix is a mixture of nearly 50 elements typically found in spent nuclear fuel, each with a mass of 100 ng. The deposited uranium ranged from 10,000 ng to 1 ng in the dried

spot residue of the 1 μL drop. These samples were used to generate a calibration plot for the uranium intensity versus the known U mass. In each case the deposit was mapped by sequentially moving the probe beam over an area larger than the visible deposit. This approach was used to ensure the entire deposit was measured. The samples were doubly sealed in Kapton film to insure no possible leaks of radioactive material.

A mock fuel rod sample was created by using an 8 mm diameter Zircaloy alloy tube, 25 mm long. Mock fuel pellets were made by mixing UO_2 and ThO_2 in known masses to generate a range of UO_2 composition within the mock fuel pellets. In this instance the uranium is a surrogate for plutonium, while the thorium is a surrogate for the typical uranium fuel matrix. The pellets were mixed with stearic acid as a binder and pressed into 8 mm diameter pellets, 2 mm thick. The pellets were loaded into the Zircaloy tube and sealed with silicone glue, then encapsulated with Kapton film.

The measurements were done on the 6-ID-D beam line of the Advanced Photon Source at Argonne National Laboratory. This beam line can produce monochromatic excitation from 50-150 keV with a $\Delta E/E = 1.4 \times 10^{-4}$ and a photon flux of 1×10^{11} photons per second at 130 keV. In this work an excitation energy of ~ 117 keV was used to effectively excite uranium above the K absorption edge of 115.591 keV. The experimental setup is shown in Figure 1. The samples were mounted on a multiple axis stage to accurately position the sample and move the sample for single point spectra, line scans and elemental maps.

The beam size was controlled by programmable slits. Elemental maps were acquired by stepping the beam over a selected area and recording a full spectrum at each point. The dried spot deposits were collected using a 500 micrometer beam spot size with a 500 micrometer step size in both x and y directions with a 5 second dwell time. The mock fuel rod was mapped using a 100 micrometer beam spot and 100 micrometer steps in x and y with a 3 second dwell time. The programmable slits allow selectable spot sizes down to 25 micrometers.

The full spectra were processed by fitting and removing the background to obtain accurate elemental intensities. Of particular concern was the overlap from the Compton scatter peak which was centered ~ 87 keV. However the wings of the Compton peak extended for 1-2 keV on either side of the centroid which needed to be removed for each spectrum processed. An example of a spectrum is shown in Figure 2. The Figure shows the measured spectrum, a model to fit the spectrum and the background. This full spectrum illustrates the separation of the typical low energy spectra normally used to characterize U at 13.6 keV compared with the UHEXRF line at ~ 98 keV used in this work. The Compton scatter peak along with the tails is visible at ~ 87 keV.

Results:

An overlay of a bare uranium spectrum with a spectrum acquired with 1.3 mm of Zircaloy shielding in front of the sample is shown in Figure 3. The Zircaloy shielding decreases the uranium signal by almost 50% and there is a significant increase in Compton scatter. However, the uranium peaks are still clearly visible, even with twice the nominal thickness of conventional nuclear fuel rod cladding. Hence the detection of uranium in typical nuclear fuel rods would be quite feasible.

An example of one of the uranium maps of the dried residue deposits is shown in Figure 4. The total uranium mass in the deposit is around 99 ng. The elemental map indicates the

residue is not uniform with several hot spots. However by summing the region of interest for the uranium peak over all the pixels in the elemental map we can obtain a summed intensity count rate for each sample. Even though a relatively small volume deposit was used, only 1 μL , the deposit covers a rather large area of almost 3 mm in diameter.

The results of the elemental maps for both the aqueous and SSF spiked dried residues is shown in Figure 5. This is a plot of the intensity (counts/sec) for each known mass of uranium in the deposit. While the aqueous and SSF matrices are quite different, the correlation coefficient for the log-log plot is ~ 0.972 . This demonstrates the quantitative analysis capability of UHEXRF, while minimizing the matrix effects.

These results have demonstrated the qualitative and quantitative capabilities of UHEXRF. However, the ability to actually characterize a nuclear fuel rod is demonstrated by scanning the mock fuel rod prepared with 8 mock fuel pellets. A picture of the mock fuel rod is shown in Figure 6. The mock fuel rod is shown with the Kapton film used to encapsulate all samples containing radioactive materials to ensure no contamination of the experimental facilities is possible. The red line on the picture indicates the successive line scans which were done to create elemental maps of the thorium and uranium inside the Zircaloy tubing. In this case the Zircaloy is a nominal 600 micrometers thick, which is typical of nuclear fuel rods. Figure 7 shows a cartoon of the mock fuel rod and the mock fuel pellets inside the Zircaloy tube. The numbers on the uranium doped pellets are the concentration of the uranium oxide mixed with the thorium oxide. Both the thorium and uranium elemental maps obtained through the Zircaloy cladding as shown below the cartoon. The elemental images provide several levels of information besides the spatial distribution of thorium and uranium. Fundamentally, the elemental maps indicate the heterogeneity of the matrix in these pellets. In real nuclear fuel the spatial distribution of the fuel element matrix should be uniform. The elemental maps show the shape of the pellets as well as spacing between the pellets. The elemental concentration of the uranium, which is the plutonium surrogate, demonstrates detection well below the nominal 1 wt% of Pu in spent nuclear fuel.

Discussion:

The results presented offer a new approach for elemental determination of spent nuclear fuel in a nondestructive manner with no sample preparation. The calibration results indicate a detection limit of around 1 ng with Zircaloy shielding and sub-nanogram levels without the shielding. The advantage of this direct elemental analysis approach is that it avoids the typical radiometric techniques which must use significant modeling of the measurement process to produce actual quantitative values. Such dependence on modeling corrections often leads to appreciable errors resulting in accuracy issues for quantitative values requiring the utmost in accuracy. UHEXRF offers a potentially more accurate direct quantitative analysis of nuclear fuel. The results with the SSF matrix indicate that even with nearly 50 elements present, there are no apparent elemental interferences with the target elements of uranium or plutonium. The elemental maps of the mock fuel rod provide insights into the potential UHEXRF offers for characterizing spent nuclear fuel. The significant aspect of this feasibility demonstration is that UHEXRF can be applied to quantification of plutonium in spent nuclear fuel. The Pu $K\alpha$ line is ~ 103 keV. The proximity of the Pu line to the U $K\alpha$ line means the quantification of Pu should be straightforward, providing a new analytical method for analyzing

nuclear spent fuel for both the matrix component as well as the key element for safeguards concerns. The elemental maps of the mock fuel rod offer the following information on the nuclear fuel pellets: through Zircaloy cladding nondestructive direct elemental measurements, uranium and thorium concentration distributions, nuclear fuel pellet homogeneity, pellet geometry and pellet orientation and gaps. These are measurements which are not currently available for either fresh or spent nuclear fuel through the Zircaloy cladding.

Conclusion:

UHEXRF has demonstrated the feasibility of nondestructively characterizing both fresh and spent nuclear fuel through the Zircaloy cladding walls. The advantages of UHEXRF offer a different approach to quantitative elemental analysis of nuclear fuel rods. These advantages include sub-nanogram sensitivity, nondestructive through container wall measurement capability, and direct, active interrogation of both fresh and spent nuclear fuel. While this demonstration has utilized synchrotron radiation, it is feasible to construct a laboratory based UHEXRF instrument with similar analytical capabilities.

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References:

1. Use of highly energetic (116 keV) synchrotron radiation for X-ray fluorescence analysis of trace rare-earth and heavy elements, Isumi Nakai, Yasuko Terada, Masayoshi Itou, and Yoshiharu Sakurai, J Synchrotron Rad. (2001) 8, 1078-1081.
2. Ultra High Energy X-ray Fluorescence: A New Paradigm for Actinide Characterization of Spent Fuel, George J. Havrilla, Michael Collins, Velma Montoya, W. T. Elam, Sarvjit Shastri, and Ali Mashayekhi, INMM 52nd Annual Meeting Proceedings, 2011.

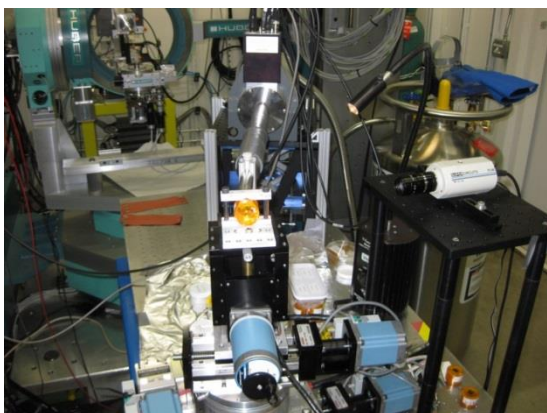


Figure 1. Experimental setup at APS 6-ID-D.

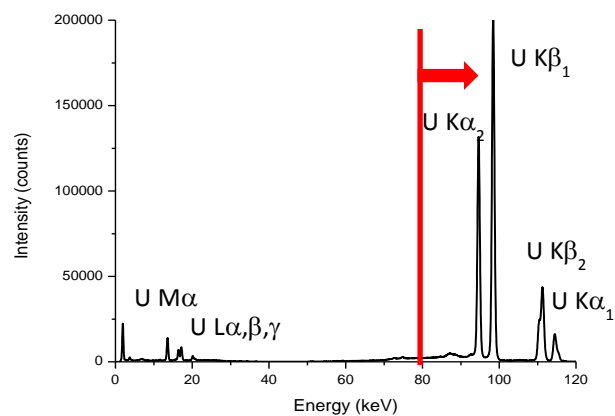


Figure 2. Complete UHEXRF spectrum of uranium dried spot residue showing both low and high energy U lines.

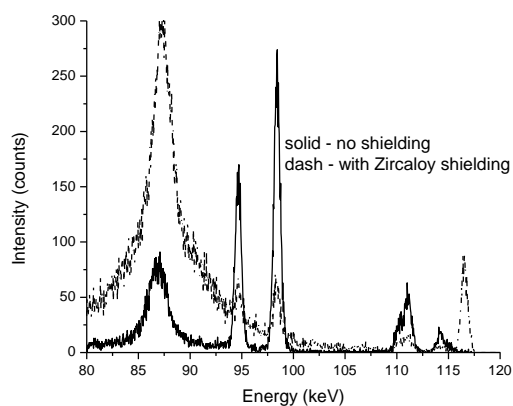


Figure 3. UHEXRF spectrum overlay for bare and Zircaloy shielded sample.

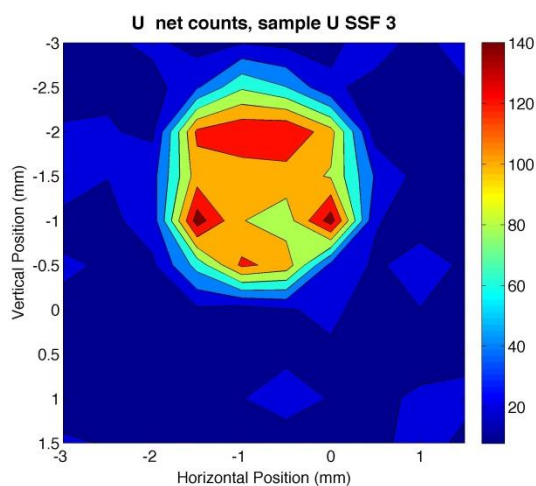


Figure 4. Elemental map of uranium deposit with SSF matrix, 99 ng U (SSF3)

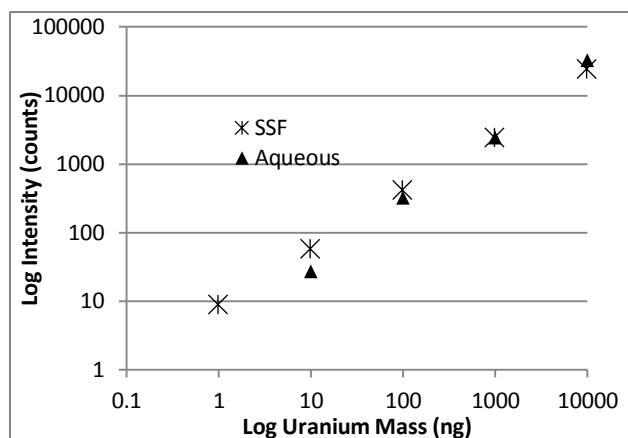


Figure 5. Calibration plot of known uranium mass with measured integrated uranium intensity from elemental maps of dried spot deposits with different matrices. Correlation coefficient for both matrices is 0.974.

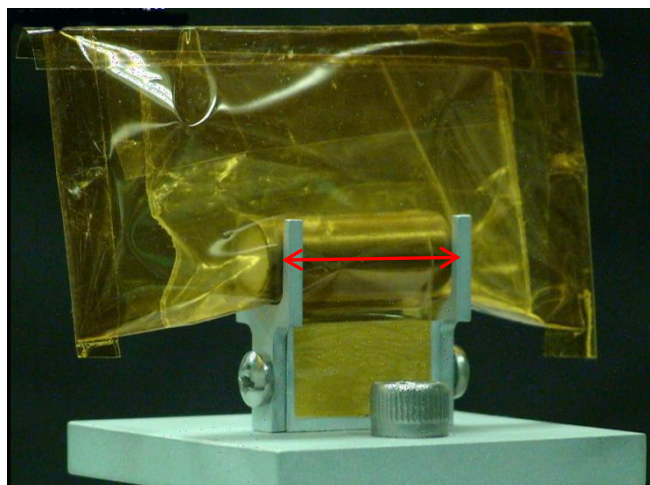


Figure 6. Picture of mock fuel rodlet in Kapton film. Red arrow indicates line scan to acquire elemental maps shown in Figure 7 for the 25 mm long rodlet.

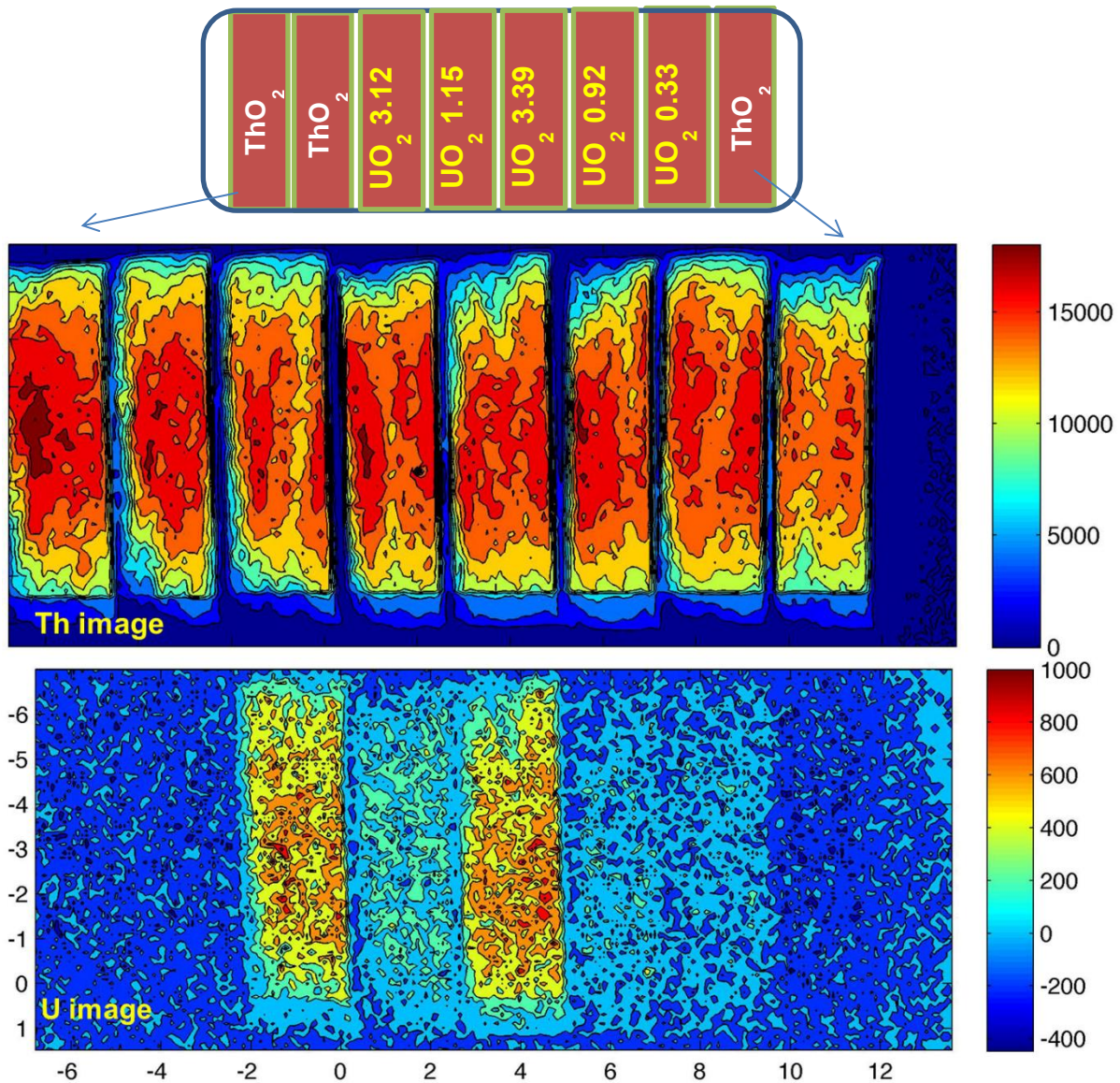


Figure 7. Cartoon of mock fuel pellets within mock fuel rod along with elemental maps of Th and U distribution through Zircaloy wall. Values with uranium oxide pellets indicate weight percent composition .